A preliminary study of small-mass radiocarbon sample measurement at Xi'an-AMS *

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Abstract: To meet the measurement demands on small-mass radiocarbon (carbon content at 10^{-6} g level) which are becoming increasingly significant, Xi'an-AMS has made improvements to the existing method of sample loading and has upgraded the Cs sputter ion source from the original SO-110 model. In order to study the feasibility of small-mass samples in Xi'an-AMS and evaluate the radiocarbon sample preparation ability using existing routine systems of H_2/Fe and Zn/Fe, the small-mass samples prepared by four different methods are tested. They are the mass division method, mass dilution method, H_2/Fe reduction method and Zn/Fe reduction method. The results show that carbon mass above 25 μg can be prepared using the existing Zn/Fe system, but no less than 100 μg is required using the existing H_2/Fe system, which can be improved. This indicates Xi'an-AMS are now able to analyze small-mass radiocarbon samples.

Key words: AMS, small-mass radiocarbon sample, ion source

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1   Introduction

Conventional decay counting and Accelerator Mass Spectrometry (AMS) are the two main analytical methods for radiocarbon [1]. Before the 1990s, decay counting was the dominant method of choice for the analysis of ^{14}C, and the techniques had been developed to the point that the sample size needed for an analysis decreased from several grams to hundreds of milligrams (the gas sample method requires only 50 mg; the liquid method, developed by Zhou Weijian, can handle a sample as small as 100–200 mg). The optimal precision of routine sample measurement can reach 2‰, and a single sample can be measured as quickly as 1–2 days. Some highly efficient laboratories could analyze around 400 samples annually [2, 3]. Since the late 1970s, however, the small sample size needed for an analysis by the decay counting methods has been significantly surpassed with the emergence and subsequent rapid development of AMS technology. The carbon mass required for a routine analysis by AMS is only about 1 mg. The time taken to complete a single-sample measurement can be less than one hour. The analysis precision of modern carbon can be better than 2‰, and over 1000 samples can be readily measured by an ordinary AMS-^{14}C laboratory [4, 5]. Therefore, it becomes essential to measure ^{14}C samples using AMS; the decay counting method is now used much less frequently.

The hundred-to-thousand-fold reduction in sample size requirement by AMS has led to wide spread applications of ^{14}C in numerous research fields such as earth science, environmental science, archeology, biosciences, marine science, cosmic chemistry and so on. Such expanding fields of research, that often require new and more difficult ^{14}C analysis, continue to push for the need to measure ever smaller sample sizes. In many scientific studies, such as analyzing the radiocarbon in the air bubbles trapped in Antarctic ice, radiocarbon dating of rock paintings, micro-dose tracing in biosciences, "microdamage" archeology, etc., one can only obtain a very tiny amount of carbon ranging from a few to hundreds of micrograms (μg) [6–9]. Many AMS laboratories abroad,

under the impetus of such demand, have started to focus on how to measure small-mass radiocarbon samples. One method is to use a gas ion source to directly measure CO_2 gas samples by AMS. This requires substantial improvement of existing solid target ion sources or the development of new gas ion sources with micro-flow controllable devices (μL/min level) [10–13]. Another method is simply to push the limit of graphite production with very small quantities of carbon, to be measured by existing solid target ion sources and AMS systems. Many laboratories have invested a great deal of effort in doing this. For example, ANSTO' scientists prepared 10–200 μg samples by improved routine method and produced about 5 μg samples by using 0.5 mL laser-heated "microfurnace"; KCCAMS can produce and measure radiocarbon samples from approximately 0.015 to 0.1 mg; the Center for Applied Isotope Studies has developed a protocol for the measurement of radiocarbon in the range of 0.01–0.3 mg [14–16]. Compared with the use of gas ion sources, making small-mass graphite provides a relatively simple approach, and it has several advantages such as stable beam intensity, higher efficiency, easy and quick sample change, low memory effect and so on [17]. There have been a number of AMS laboratories abroad undertaking small-mass radiocarbon research, but a similar effort is currently still lacking in China, which has limited Chinese scientific research in certain areas.

This article will discuss the preliminary study on the feasibilities of carrying out routine small-mass radiocarbon sample measurement at Xi'an-AMS using the existing main equipment. We will present the result of a systematic assessment test, and identify the areas where further improvements are required.

2   Ion source and sample loading for small-mass radiocarbon sample measurement

The measurements of small-mass radiocarbon samples were carried out using the 3 MV AMS system at the Xi'an-AMS Center, IEECAS. The key point for small-mass radiocarbon sample measurement is not only a suitable ion source system, but also a powerful sample loading.

2.1   Ion source

The ion source system is often a key factor in determining whether small-mass radiocarbon samples can be measured. Compared to measuring more regularly sized samples, the measurement of small-mass samples could face some difficulties such as lower currents and elevated memory effect. Those laboratories pursuing this direction often found it necessary to first carry out certain upgrades to their ion sources [15]. Xi'an-AMS uses a Cs sputter ion source of the SO-110 model from HVEE (High Voltage Engineering Europa), which is a major upgraded version from the manufacture's original design of 2008 [18] (See Fig. 1(a)). The improved new ion source shown in Fig. 1(b) has its own distinctive character: the open structure around the ionizer and sample leads to better vacuum, an extra coolant loop is added to the ionizer supporting base, the halos surrounding the Cs^+ focusing spot are eliminated by shaping the edge of the ionizer central hole, the improved insulation structure provides full protection to the insulator. The new ion source's electrostatic and mechanical performance are more stable as a result of its improved pumping speed
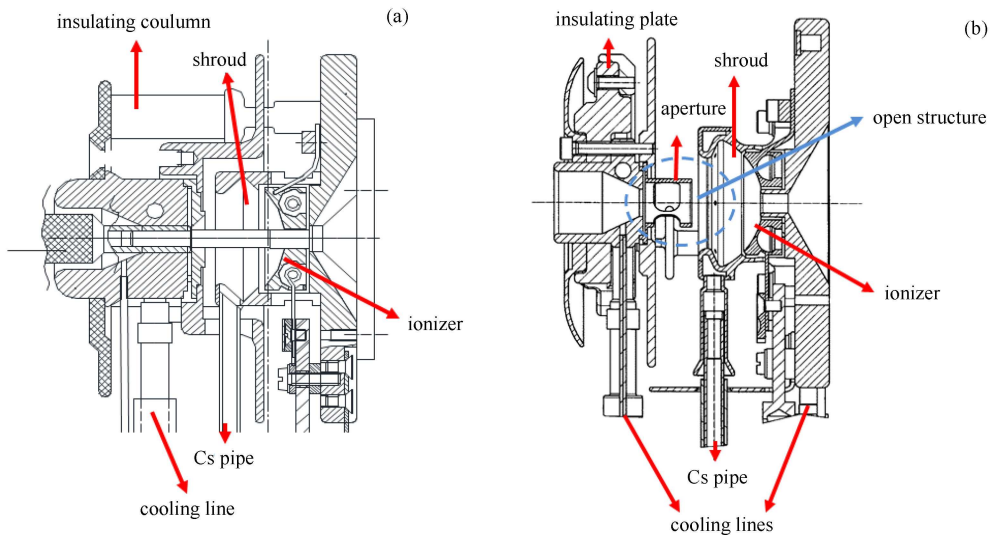

Fig. 1.   (color online) (a) Schematic diagram of the original ion source; (b) Schematic diagram of the improved ion source.

and carefully modeled temperature gradient throughout the ion source assembly, all of which result in low cross contamination, which is essential for small-mass radiocarbon measurement.

Before doing test measurements with small-mass radiocarbon samples, we first performed a SO-110 Cs^+ spot simulation using Simion 8.0 and an actual Cs^+ measurement using a 3 mm graphite rod target pressed into a 3 mm diameter bore hole in a detachable aluminum target cap (Holder/Cathode). Fig. 2(a) shows that Cs^+ beam has a poor focusing performance due to Simion's limitation of not including space charge calculation and lack of resolution on the ionizer's spherical surface, but from Fig. 2(b), we can see that the Cs^+ spot actually has a diameter of 1.1 mm (the black area within the pale yellow dashed circle). The red dotted circle would be the regular sample size of 1.3 mm-diameter. If a small-mass sample is packed into a 1 mm-diameter hole, it should be fully sputtered, leading to higher utilization efficiency for the sample material. The spot center had a small offset,

which can be corrected by careful ionizer assembly using a filler gauge.

2.2   Sample loading

The mass and size of small-mass samples are less and far smaller than those of routine samples. This leads to difficulties in loading the sample into the holder [14]. The sample loading is completed using our designed and patented powder sample loading tool [19] (Fig. 3). Fig. 3(a) shows the original sample loading and pressing tool, with which the powder sample is fed from the bottom of the fill, requiring many parts to be assembled to form a mold. After pressing one target, all parts of the device must be disassembled, cleaned, and reassembled again for the next target. The extrusion-needle is at the top of the press machine so that the direct impacts punch the extrusion-needle downward, thereby forming a sample mold. This process makes a direct impact on the long skinny extrusion-needle used, which is easily
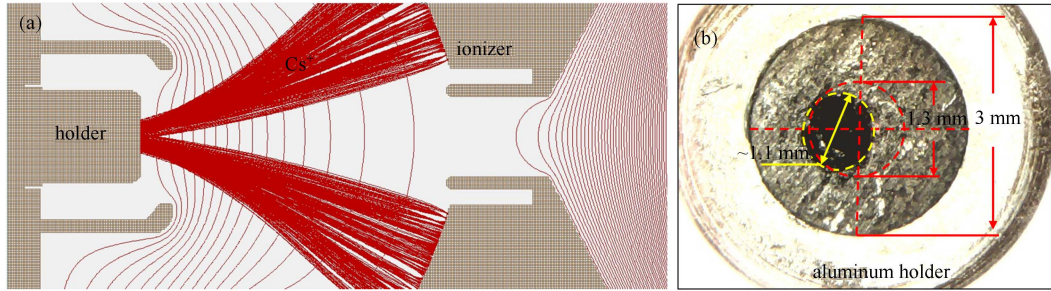

Fig. 2.   (color online) (a) Simulation of Cs^+ beam bombardment of partial enlargement; (b) Cs^+ beam bombardment 3 mm graphite rod target.
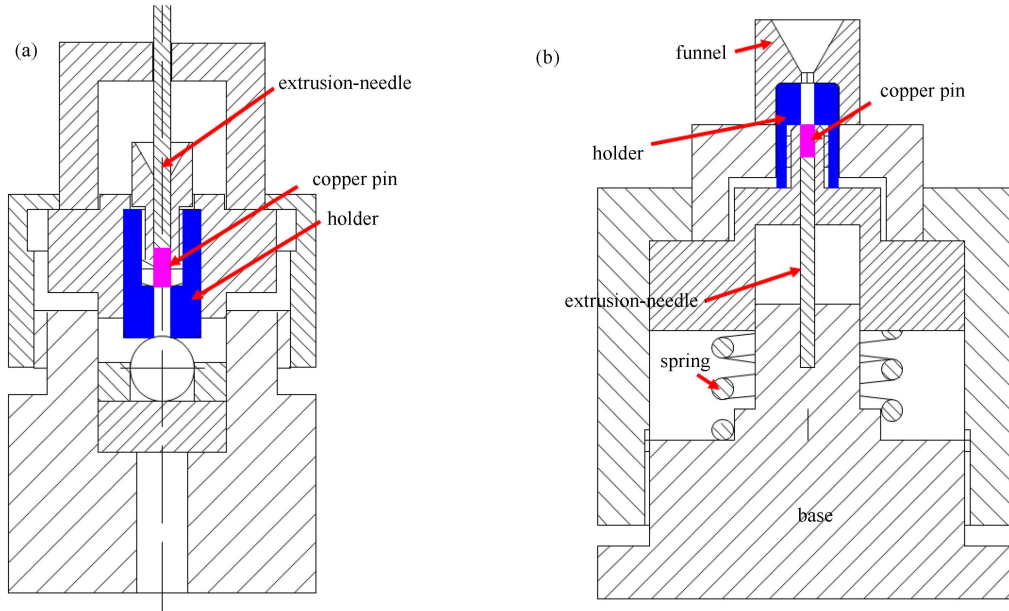

Fig. 3.   (color online) (a) Original tool of sample loading and pressing; (b) Redesigned tool of sample loading and pressing.

damaged. Also, when filling the powder, one could not observe the volume of the powder filled, easily causing mold rejection due to too much or too little sample in the holder. From Fig. 3(b), we can see the redesigned sample loading and pressing tool which overcomes the disadvantages of the original method by reversing the mold; that is, powder is filled from the top, using the backward extrusion to improve the efficiency of forming the mold and to reduce wear on the plunger chip and extrusion-needle and also minimize the waste of sample material. The new method is particularly suitable for loading samples into small bore holes to simplify the handling of small-mass samples and to guarantee optimum sample density and surface finish for best ion source performance.

The redesigned sample loading device has made packing small-mass samples much easier to operate, but ultra small-mass sample loading is still extremely difficult to handle. Although one could consider increasing the proportion of the catalyst Fe powder, it is still very difficult to work with an ultra small amount of CO_2. Therefore, we attempt to directly press Fe powder into a copper holder first, which is then to be used directly in the reduction reaction, avoiding the difficulty of filling the powder into a tiny hole after. Main reduction reaction of ultra small CO_2 gas is then performed at the holder surface by the catalyst Fe powder. A copper holder is chosen instead of a routine aluminum holder for its higher melting point, because the holder is sealed in a quartz tube heated during the reduction process.

The improved SO-110 ion source, sample loading method and small bore hole holders were used in the measurements of small-mass samples in this work. Other operating parameters and the descriptions of Xi'an-AMS can be found in reference [5].

3 Preparation of small-mass radiocarbon samples[1])

The analysis of small-mass radiocarbon samples was done using the following 4 different methods.

1) Mass division method. The sample is prepared by the routine method to obtain conventional mg level graphite, which is then directly divided into small-mass samples of different mass (including 9 CSC samples from 20 μg to 545 μg). Different amounts of Fe powder are filled into the bottom of a holder as the carbon mass is successively reduced. Because the graphitization is done with regular amount of CO_2, this method avoids possible preparation problems of small-mass radiocarbon, so it provides a relatively independent study on the measurement quality of small-mass radiocarbon samples using

the Xi'an-AMS system. The problem with this method is that it is hard to handle a few micrograms of extremely small-mass samples.

2) Mass dilution method. The sample is still prepared by the routine method to obtain conventional mg level graphite. Then the sample is divided into several parts and mixed with Fe powder in different proportions. The advantage of this method is that it is easy to obtain ultra small-mass radiocarbon samples (including 5 CSC samples from about 2 μg to 55 μg and 8 blank samples from about 7 μg to 531 μg) and at the same time to avoid the complications in the graphitization process of a small amount of CO_2. The beam intensity of this sample is close to the real situation of a directly reduced ultra small-mass sample, which mimics the performance of the Xi'an-AMS system when beam intensity is low. The simulated ultra small-mass sample is accumulated on the top surface of the holder with an area smaller than Cs^+ spot, leading to the sample being almost fully utilized, thus the real blank limitation of ultra small-mass samples can be derived.

3) Direct preparation by the H_2/Fe reduction method. The existing routine H_2/Fe reduction method and system are directly used to prepare small-mass radiocarbon (including CSC samples and background blank samples of 50 μg, 100 μg, 500 μg, respectively). The advantage of the H_2/Fe method is its shorter reduction reaction time than the Zn/Fe method; the contamination possibility during preparation is minimized. This is the prime method used for small-mass radiocarbon preparation in the current study. The original samples (prior to division or dilution) used in the studies of method 1) and 2) are both prepared by the H_2/Fe method.

4) Direct preparation by the Zn/Fe reduction method. The existing routine Zn/Fe semi-automatic systems have 24 lines for reduction that have been established with assistance from the University of Arizona. The Zn/Fe method is performed using Zn and TiH_2 as reductants in a few labs [15], but in our small-mass radiocarbon preparation the Zn quantity is adjusted to be 30 mg and the Fe/C ratio is far more than the regular 2/1. Various samples under 100 μg were prepared using the existing Zn/Fe system, including 4 OX Ⅱ samples from 50 μg to 68 μg and 3 same known-samples of the FIRI code 'C' (the Fourth International Radiocarbon Inter-Comparison) from 25 μg to 50 μg.

Fe powder is also a key factor for the measurement of small-mass radiocarbon samples; therefore we experimented with different Fe powders so that we could choose the best for the purpose. In addition, we prepared special types of small-mass radiocarbon samples by means of

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1) Note: The regular mg level samples are prepared and measured by AMS at the same time. CSC is China Sugar Carbon standard, Anthracite is blank sample, OX Ⅱ is New Oxalic standard.

Fe powder directly pressed in copper holders for their direct use in reduction reactions. All details will be discussed in the next section.

4   Result and discussion

Four kinds of small-mass samples were measured at Xi'an-AMS[1]. Fig. 4 shows the pMC (percent Modern Carbon) values (a), the average $^{12}C^{3+}$ beam intensity (b), $^{13}C/^{12}C$ (c) and $(^{14}C/^{12}C)/(^{13}C/^{12}C)^2$(d) of CSC standards by different preparation methods using H_2/Fe system with mass from a few to hundreds of micrograms. From Fig. 4, the pMC of the 'Mass division method' of the CSC standards are relatively stable, and only slightly decline with the decrease in mass, and the $^{12}C^{3+}$ intensity obviously decreases with mass but still stays above 8 μA at least. Sample sizes are separated into smaller mass range using 'Mass dilution method'. The pMC are slightly wavy at the beginning and consistent with pMC values of the 'Mass division method' above 20 μg range, then acutely decrease with mass under 20 μg; the $^{12}C^{3+}$ intensity almost has the same tendency. This demonstrates that the pMC and beam intensity suffer severe decline with the decrease of sample size, especially when it is approaching 20 μg. Minami et al. explain that this is caused by varying isotopic fractionations due to differences in graphitization yield and target thickness [20], but in the measurements described here, the original samples were obtained by routine preparation methods with typical mg mass, which were just divided or diluted by extra Fe powder mechanically. Fig. 4(b) indicates that the beam intensity obviously decreases along with sample size; this phenomenon is particularly evident at ultra small-mass under extreme low beam conditions. This implies that pMC has a certain correlation with beam intensity, which will be studied in the next experiments. From Fig. 4, we can see the results of direct preparation by the H_2/Fe reduction method of sample mass of 500 μg, 100 μg and 50 μg. The pMC of 500 μg and 100 μg samples are consistent with the preceding methods, and $^{12}C^{3+}$ beam intensities also decline with mass. Then, the 50 μg sample has a huge deviation from the normal value. This sample gave no $^{12}C^{3+}$ beam (only equivalent to charge digitizer noise) and few ^{14}C counts (few counts which can be expected from pure Fe powders) during AMS measurement; therefore, the so-called 50 μg sample actually had no carbon in it. It is a result of low graphitization yield and lack of pressure measurement sensitivity in the chemical preparation process when CO_2 pressure runs too low. From Fig. 4(c) and (d), we can see that the trend of $^{13}C/^{12}C$ ratio is a mirror image of pMC and the ratio of $(^{14}C/^{12}C)/(^{13}C/^{12}C)^2$ also has the same trend as pMC. However, $^{13}C/^{12}C$ ratios of 100 and 500 μg directly prepared samples are slightly lower than the division samples of similar mass, and 50 μg sample failed also in Fig. 4(c) and (d). Consequently, the sample less than 100 μg is not doable using the existing routine H_2/Fe system; we need to improve this system in the next step. The experimental results indicate that the small-mass samples should be calibrated to standards of the same carbon content level. In future analysis, small-mass samples and standards for normalization will be grouped by different mass ranges, to be analyzed in the same batch together. The sample mass can be roughly divided into ranges of <20 μg, 20–80 μg, 80–300 μg and >300 μg.

The blank samples were obtained by two methods. Fig. 5 shows the pMC (a), the average beam intensity (b), $^{13}C/^{12}C$ (c) and $(^{14}C/^{12}C)/(^{13}C/^{12}C)^2$ (d) of Anthracite blank samples versus sample size. As mentioned above, the limitation to the ultra small-mass sample measurement blank can be assessed using 'Mass dilution method' samples, and the real situation for the existing chemical preparation system can be reflected by the directly prepared samples. Fig. 5(a) shows the results for sample sizes from about 7 μg to 531 μg (compared to CSC samples, the blanks made by the dilution method can span a larger mass range from a few micrograms to half milligrams). With the reduction of sample size, the pMC increases gradually. We can regard it as the way to assess the size limitation to the small-mass samples (it is deducible that the actual directly prepared ultra small-mass blank samples will be worse than what can be accounted for just from the measurement using the Xi'an-AMS system). The minimum blank sample size that can be ^{14}C dated is 7.5 μg, to correspond with 34607±703 a BP. Fig. 5 also shows the results of direct preparation by the H_2/Fe reduction method of samples 500 μg, 100 μg and 50 μg, and a 900 μg regular blank sample. Obviously, the pMC results of directly prepared samples are slightly higher than the same mass sizes by the dilution method samples, but they have the same trend. Fig. 5(c) indicates that two directly prepared samples of ⩽500 μg are slightly lower than the dilution samples of similar mass. We can learn from Figs. 4(c) and 5(c) that isotopic fractionation was caused by small-mass chemical preparation processes in the existing H_2/Fe system. From Fig. 5(d), we can see that the $(^{14}C/^{12}C)/(^{13}C/^{12}C)^2$ also has the same trend as pMC. The 50 μg blank sample of direct preparation by the H_2/Fe reduction method also failed.

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1) Note: The pMC of the division and dilution method samples were calibrated by regular standard as unknown samples. The $^{12}C^{3+}$ beam intensity of regular analysis is typically between 30–40 μA at Xi'an-AMS.
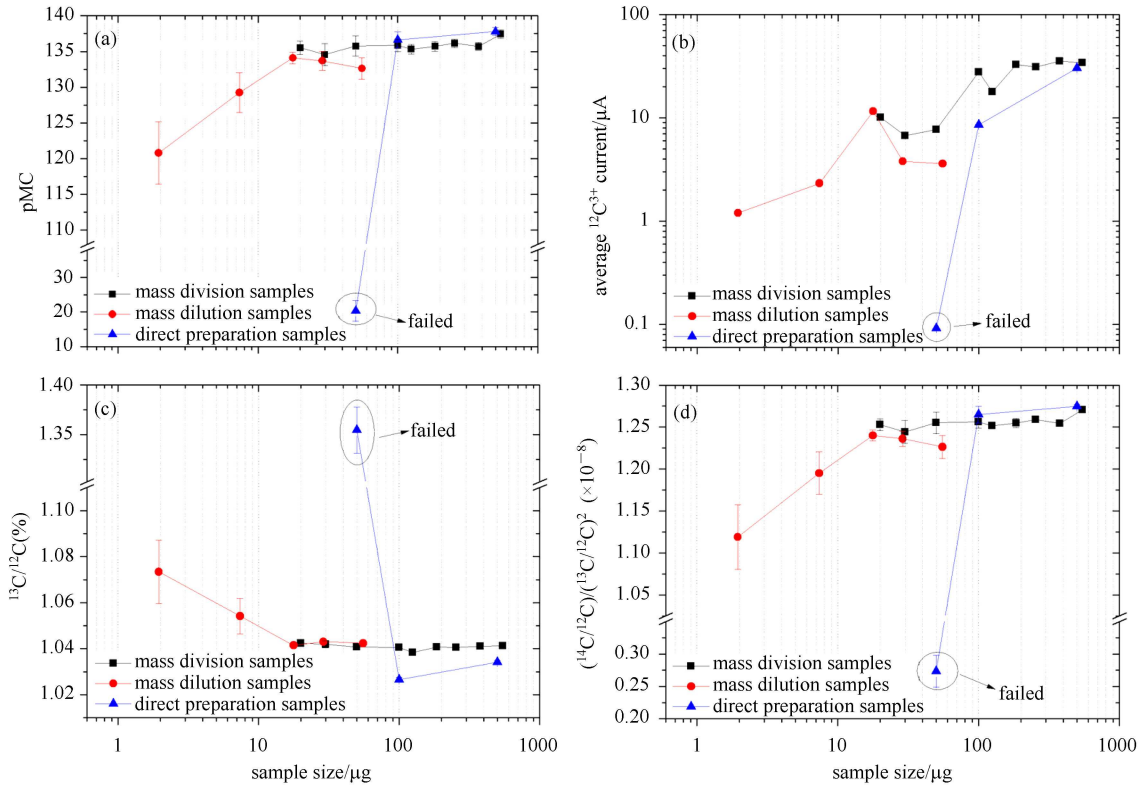
Fig. 4.   (color online) The pMC values (a), the average beam intensity (b), $^{13}C/^{12}C$ (c) and $(^{14}C/^{12}C)/(^{13}C/^{12}C)^2$ (d) of CSC standards by different methods versus sample size.
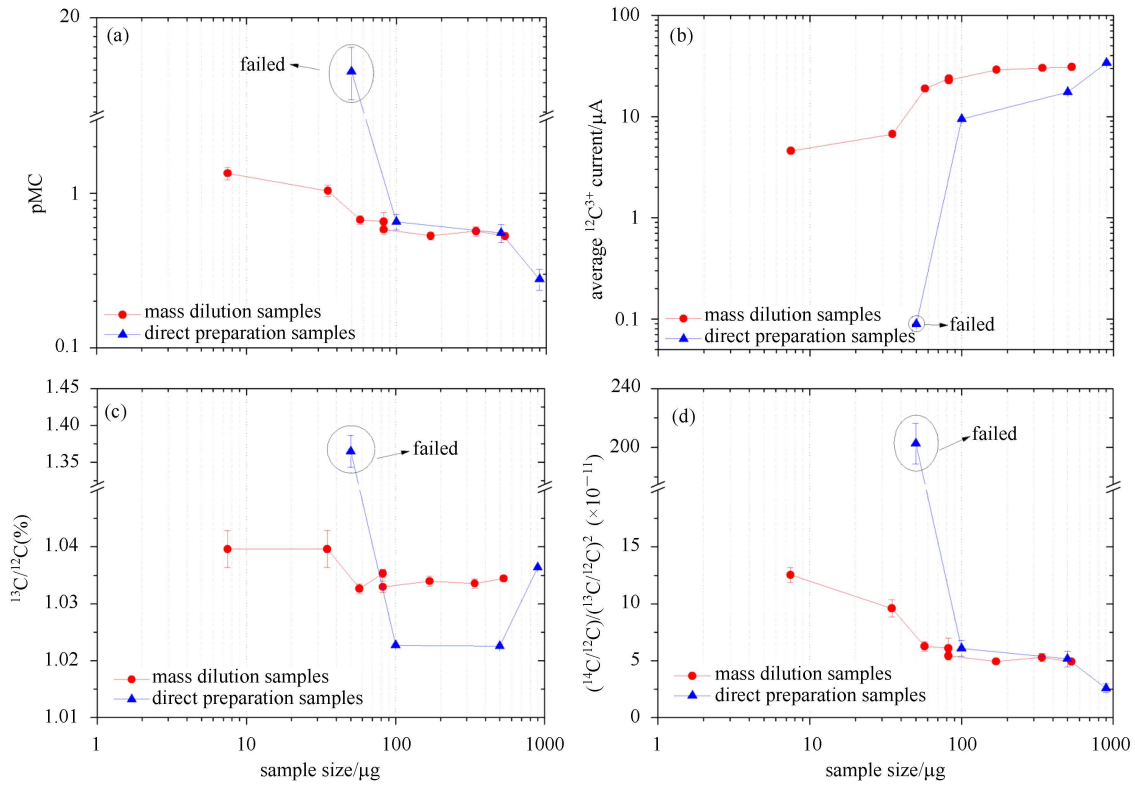

Fig. 5.   (color online) The pMC values (a), the average beam intensity (b), $^{13}C/^{12}C$ (c) and $(^{14}C/^{12}C)/(^{13}C/^{12}C)^2$ (d) of Anthracite blanks by different methods versus sample size.

Figure 6 shows the pMC of small-mass OX II standards and known samples prepared by the Zn/Fe system using small-mass standards calibration with sample size. Only samples under 100 µg are discussed here. The known samples were prepared from the preserved sample of the FIRI code 'C' sample. The population mean of this known sample is 18132±245 a and AMS mean is 18175±135 a [21]. From Fig. 6, we can see that the pMC of OX II standards are stable and the known samples are consistent within 1σ, but the error increases relatively, with the measurement time being just 300 seconds, far less than the normal measurement time. Table 1 shows the results of standards and known samples using different calibration methods. From Table 1, our results of small-mass samples and the reported value are consistent within the error. Therefore, the existing Zn/Fe system has the ability to prepare small-mass samples above 25 µg.
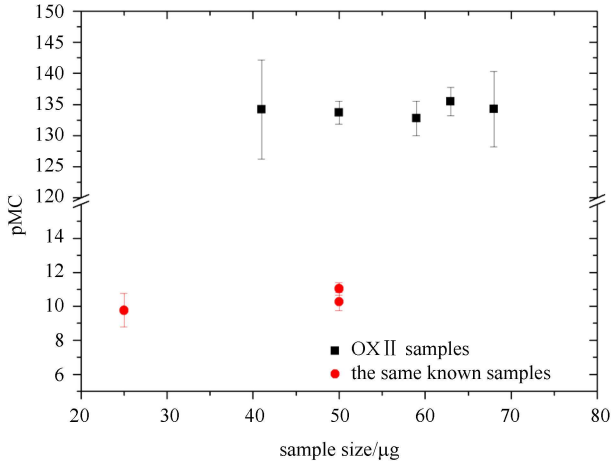

Fig. 6.   (color online) The pMC values of small-mass OX II standards and known samples prepared by the Zn/Fe system using small-mass standards calibration versus sample size.

In addition to the above four kinds of small-mass sample preparation methods studied, the effects of different Fe powders were also studied. The impact of Fe powder can almost be ignored for measurement of regular mg sized samples, but with the decrease of sample size, the influence of Fe powder increases gradually. Therefore, choosing the right Fe powder catalyst is crucial to small-mass samples measurement. We experimented with routinely used domestic Fe powder of 99% purity and the Sigma-Aldrich 99.995% Fe_2O_3 (SA Fe_2O_3). Those powders were reduced by H_2 or directly pressed into a holder. In 300 seconds, 22 ^{14}C counts can be detected using routine Fe powder reduced by H_2, approximately 0.073 atoms/sec; 9 ^{14}C counts in 300 s can be detected from SA Fe_2O_3 reduced by H_2, approximately 0.030 atoms/sec; the sample of directly pressed SA Fe_2O_3 in a holder gives no ^{14}C count in 300 s. (Note: a routine modern radiocarbon standard sample gives ^{14}C counting rate of about 100 atoms/sec.) Obviously, SA Fe_2O_3 is better than currently used domestic Fe powder. In the next step, we will study more catalyst material so that a suitable catalyst for small-mass sample measurement can be found for both high purity and low cost. The ^{14}C counting rate from SA Fe_2O_3 reduced by H_2 is higher than that from directly pressed SA Fe_2O_3 due to vacuum limitations of the H_2/Fe system or H_2 purity. This means that the ultra small-mass samples are not doable using the existing H_2/Fe system.

Furthermore, two samples of Fe powder were directly pressed in copper holders for direct use in reduction reactions. The $^{12}C^{3+}$ beam intensity of XAT0120 (500 µg) is slightly more than $1/9^{th}$ that of a regular massed sample, and the same is true for XAT0121 (300 µg). These results show that the beam intensities of this method are smaller than those of similar sized samples prepared by other methods. The main reason is that reaction is limited to the limited pressed target surface area only.

Table 1.   The AMS results of small-mass standard and known samples preparation by Zn/Fe system using different calibration method[1].

| target No. | description of sample | mass/ µg | regular size standard calibration | | | | small-mass standard calibration | | | |
| | | | pMC | | ^{14}C age (a BP) | | pMC | | ^{14}C age (a BP) | |
			pMC	error (1σ)	^{14}C age	error (1σ)	pMC	error (1σ)	^{14}C age	error (1σ)
XAT0107	OX II	63	133.03	2.33	—	—	135.45	2.28	—	—
XAT0108	OX II	59	130.38	2.81	—	—	132.75	2.79	—	—
XAT0109	OX II	41	131.78	7.80	—	—	134.17	7.97	—	—
XAT0110	OX II	50	131.32	1.93	—	—	133.71	1.85	—	—
XAT0111	OX II	68	131.87	5.93	—	—	134.26	6.04	—	—
XAT0116	known sample	25	9.59	0.98	18832	780	9.76	1.00	18690	781
XAT0117	known sample	50	10.84	0.36	17849	263	11.03	0.36	17707	261
XAT0118	known sample	50	10.09	0.52	18427	407	10.27	0.53	18284	406
XAT0116-0118 mean value			10.17	0.25	18360	196	10.35	0.25	18218	192

Note: 1) In Table 1, the regular sized standard samples used were measured in the same batch with small-mass standard and the known samples.

After reduction reactions were completed we observed the black powder adhering to the quartz tube wall, which was considered to be the 'excess' carbon not able to combine with Fe powder. Probably for ultra small-mass samples carbon could completely combine with the Fe powder, because in this case the carbon content is far smaller than the reduction capacity of the pre-pressed Fe surface. The results show that $^{14}C/^{12}C$ is about 1.379×10^{-12}, $^{13}C/^{12}C$ is about 1.0287×10^{-2}, $^{12}C^{3+}$ is about 3.8 μA, which are similar to the regular sized CSC samples ($^{14}C/^{12}C$ is about 1.417×10^{-12}, $^{13}C/^{12}C$ is about 1.0397×10^{-2}, $^{12}C^{3+}$ is about 32 μA). All these samples were measured similarly in a 200 s quick preliminary test batch. Therefore, this method is feasible. However, we need to study the impact on the ^{14}C background from the copper holders entering the reduction reactions and to further improve the H_2/Fe system for ultra small-mass samples.

5   Conclusion and future plans

According to the experimental results and analysis the following conclusions can be drawn:

1) Xi'an-AMS has the ability to measure small-mass radiocarbon samples, after it has improved the sample loading method and upgraded the ion source that provided the feasibility foundation for the analysis. In order to utilize the small-mass samples more efficiently, the 1 mm-diameter holder will be used. In future, the ^{12}C

and ^{13}C dark current influence on measurement will be further investigated.

2) The method of Fe powder being directly pressed in copper holders for direct use in reduction reactions is suited for handling ultra small-mass samples and to avoid loading, but the effect on the ^{14}C background must be evaluated and the procedures optimized in the next step.

3) Small-mass radiocarbon samples are best calibrated with standards at closer carbon content levels for AMS measurement.

4) Small-mass radiocarbon samples of mass less than 100 μg cannot be prepared using the existing H_2/Fe system. In future, we will build a new one or improve the existing system. Basically the reduction-unit needs to be redesigned as follows: First, improve the vacuum of the system; secondly, increase the pressure sensor sensitivity, and reduce the volume of the reaction tube; furthermore, choose more pure reagents and so on to achieve ultra/small-mass radiocarbon sample preparation.

5) Small-mass radiocarbon samples above 25 μg can be prepared by the existing Zn/Fe system, which can satisfy the preparation of the majority of the small-mass samples. However, this system needs to be improved further for ultra small-mass sample preparation. The reduction tube volume needs to be reduced by half and the pressure sensor needs to be replaced with a more accurate and more sensitive one. It can be expected that ultimate measurable small carbon mass can break 10 μg.

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